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Electronic absorption spectra of meta and para-aminophenols

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The near ultraviolet absorption spectra of meta- and para-aminophenols in the vapour phase have been recorded and measured. With the help of the Raman and Infra red spectra data of these isomers available in the literature, the spectra are analysed. The results obtained are reported and discussed.

1. INTRODUCTION

The vibrational spectra of ortho-, meta- and para-aminophenols have been studied by Verma & Rai (1970). The electronic absorption spectrum of ortho-aminophenol has been studied by Sharma & Rao (1963). In further continuation of our work on the ultavriolet absorption spectra of some substituted benzenes, the electronic absorption spectra of meta- and para-aminophenols have been recorded in the vapour phase and analysed. The results are here reported and discussed.

2. EXPERIMENTAL

Pure samples of these compounds which are solid at room temperature were further purified and used. Vapour phase spectra were recorded on a Hilger-Littrow spectrograph with path lengths varying from 25 to 200 cms and at temperatures ranging from 0 to 200°C. The accuracy of measurements has been estimated to be $\pm$ 5 cm^{-1} for sharp bands and $\pm$ 10 cm^{-1} for broad or diffuse bands.

3. RESULTS AND DISCUSSION

The spectra of both the molecules lie approximately in the region 2800 Å to 3200 Å. The bands are rather sharp and degraded to the red. The wave number of the bands their intensities and the proposed assignments for the two molecules are given in Tables 1 and 2.

Most of the bands of meta-aminophenol could be accounted for in terms of 6 ground state fundamentals 229, 266, 367, 535, 620 and 852 cm^{-1}; 13 upper state fundamentals 167, 206, 206, 345, 508, 564, 835, 944, 1042, 1124, 1165, 1229, 1272 and 1537 cm^{-1} and three difference frequencies 24, 40 and 60 cm^{-1}, whereas with bands obtained in para-aminophenol could be accounted for in terms of 6 ground state fundamentals 226, 358, 368, 503, 528 and 581 cm^{-1}; 14 excited

Table 1. Prominent absorption bands of meta-aminophenol

Wave number (cm^{-1}) and Intensity	Assignment
33258 w	0, 0 − 852
33375 w	0, 0 − 2 × 367
33490 w	0, 0 − 620
33575 w	0, 0 − 535
33621 w	0, 0 − 229 − 266
33743 m	0, 0 − 367
33844 m	0, 0 − 266
33881 m	0, 0 − 229
33988 m	0, 0 − 2 × 60; 0, 0 − 3 × 40
34030 m	0, 0 − 2 × 40
34050 m	0, 0 − 266 + 206
34061 m	0, 0 − 2 × 24
34086 s	0, 0 − 229 + 206
34110 s	0, 0
34204 w	0, 0 + 944 − 852
34265 w	0, 0 + 2 × 345 − 535
34277 m	0, 0 + 167
34316 m	0, 0 + 206
34421 w	0, 0 + 944 − 535
34445 m	0, 0 + 345
34504 m	0, 0 + 1229 − 852
34531 m	0, 0 + 1272 − 852
34618 m	0, 0 + 508
34674 m	0, 0 + 564
34766 w	0, 0 + 1272 − 620
34801 m	0, 0 + 2 × 345
34873 m	0, 0 + 1124 − 367
34909 w	0, 0 + 1165 − 367
34945 m	0, 0 + 835
35054 m	0, 0 + 944
35099 w	0, 0 + 1537 − 535
35124 m	0, 0 + 2 × 508
35152 m	0, 0 + 1042
35189 m	0, 0 + 508 + 564
35234 m	0, 0 + 1124; 0, 0 + 2 × 564
35275 m	0, 0 + 1165
35339 m	0, 0 + 1229
35382 m	0, 0 + 1272
35413 w	0, 0 + 2 × 835 − 367
35637 w	0, 0 + 1537
35786 w	0, 0 + 2 × 835
35854 w	0, 0 + 1229 + 508
35948 w	0, 0 + 1272 + 564
36023 w	0, 0 + 2 × 944
36102 w	0, 0 + 1165 + 835
36184 w	0, 0 + 2 × 1042; 0, 0 + 1229 + 835
36280 w	0, 0 + 1229 + 944
36362 w	0, 0 + 2 × 1124
36558 w	0, 0 + 2 × 1229
36619 w	0, 0 + 3 × 835; 0, 0 + 1229 + 1272
36886 w	0, 0 + 1229 + 1537
36915 w	0, 0 + 3 × 944; 0, 0 + 1229 + 1537

Table 2. Prominent absorption bands of para-aminophenol

Wave number (cm^{-1}) and Intensity	Assignment
30812 w	0, 0 − 581
30860 w	0, 0 − 528
30890 w	0, 0 − 503
31025 w	0, 0 − 368
31035 w	0, 0 − 358
31167 w	0, 0 − 226
31180 w	0, 0 − 3 × 72
31248 m	0, 0 − 2 × 72
31273 w	0, 0 − 4 × 30
31302 m	0, 0 − 3 × 30
31321 s	0, 0 − 358 + 284
31331 m	0, 0 − 2 × 30
31362 s	0, 0 − 503 + 473
31393 s	0, 0
31414 ms	0, 0 + 522 − 503
31448 m	0, 0 + 284 − 226
31458 m	0, 0 + 436 − 368
31565 m	0, 0 + 172
31600 m	0, 0 + 436 − 226
31640 m	0, 0 + 473 − 226
31657 m	0, 0 + 798 − 528
31677 m	0, 0 + 284
31694 m	0, 0 + 301
31742 w	0, 0 + 935 − 581
31804 w	0, 0 + 935 − 528
31829 m	0, 0 + 436
31866 m	0, 0 + 473
31915 m	0, 0 + 522
32043 w	0, 0 + 1183 − 528
32152 m	0, 0 + 1250 − 503
32191 m	0, 0 + 798
32265 m	0, 0 + 2 × 436
32305 m	0, 0 + 473 + 436
32328 m	0, 0 + 935
32342 m	0, 0 + 2 × 473
32390 w	0, 0 + 522 + 473
32418 m	0, 0 + 1025
32440 w	0, 0 + 1550 − 503
32459 m	0, 0 + 1066
32570 m	0, 0 + 1183
32625 m	0, 0 + 1232
32643 m	0, 0 + 1250
32674 w	0, 0 + 798 + 473
32699 w	0, 0 + 3 × 436
32800 w	0, 0 + 935 + 473
32813 w	0, 0 + 3 × 473
32895 w	0, 0 + 1066 + 436
32910 w	0, 0 + 1025 + 473
32943 w	0, 0 + 1550
32989 w	0, 0 + 2 × 798

Table 2—Contd.

Wave number (cm^{-1}) and Intensity	Assignment
33053 w	0, 0+1183+473
33099 w	0, 0+1232+473
33115 w	0, 0+1250+473
33166 w	0, 0+1250+522
33216 w	0, 0+1025+798
33251 w	0, 0+1066+798
33263 w	0, 0+2×935
33285 w	0, 0+4×473
33341 w	0, 0+1250+798
33359 w	0, 0+1025+935
33380 w	0, 0+1183+798
33415 w	0, 0+1550+473
33426 w	0, 0+2×798+436; 0, 0+1232+798
33435 w	0, 0+1250+798
33458 w	0, 0+2×1025
33485 w	0, 0+1025+1066
33525 w	0, 0+2×1066
33559 w	0, 0+1232+935
33581 w	0, 0+1250+935
33604 w	0, 0+1183+1025
33642 w	0, 0+1183+1066
33677 w	0, 0+1250+1025; 0, 0+1232+1066
33755 w	0, 0+2×1183
33792 w	0, 0+3×798
33826 w	0, 0+1250+1183
33862 w	0, 0+2×1232
33900 w	0, 0+2×1250
33977 w	0, 0+1550+1025
34010 w	0, 0+1550+1066
34127 w	0, 0+1550+1183
34160 w	0, 0+1550+1232
34191 w	0, 0+3×935
34296 w	0, 0+3×798+522
34326 w	0, 0+436+2×1250
34377 w	0, 0+473+2×1250
34592 w	0, 0+3×1066

state fundamentals 172, 284, 301, 436, 473, 522, 798 935, 1025, 1066, 1183, 1232, 1250 and 1550 cm^{-1} and two difference frequencies 30 and 72 cm^{-1}.

The assignment of the vibronic bands and the nature of the observed electronic transitions in the two molecules are discussed in the following paragraphs :

Assuming planar structure for the two molecules and treating the -OH group as a single mass point para-aminophenol will belong to the point group C_{2v} while the meta-isomer will have the C_s point group symmetry. However, for the normal structure of the -OH group the symmetry will be C_s in both the isomers. The forbidden electronic transition A_{1g}–B_{2u} of benzene becomes an

allowed A_1–B_2 transition in C_{2v} symmetry and A'–A' in C_s symmetry of the isomeric aminophenols. The spectrum should exhibit the characteristics of an allowed transition, a strong 0, 0 band and the totally symmetric a_1 type (in C_{2v}) or a' type (in C_s) would be strongly excited. The a' or b_1 and b_2 type vibrations will occur with weak transition moment.

The strong band on the longer wavelength side at 34110 and 31393 cm^{-1} has been chosen as the 0, 0 band in meta- and para-aminophenols respectively. The spectra have been analysed with the help of the analysed Raman and Infrared spectra of these molecules reported in the literature. Under C_{2v} symmetry the 30 vibrations of the phenyl nucleus of the para-isomer will belong to $8a_1+6a_2+9b_1+7b_2$ type while under C_s symmetry there will be $21a'$ and $9a''$ type of vibrations.

The excited state fundamentals 835, 944 and 798, 935 cm^{-1} in meta- and para-aminophenols are very prominent. However the corresponding ground state frequencies could not be obtained even at higher vapour pressures. The infrared bands at 848, 1010 cm^{-1} and 848, 1015 cm^{-1} in meta- and para-aminophenols respectively can be taken to represent the ground state vibration corresponding to 835, 944 and 798, 935 cm^{-1} in the excited state. They combine with most of the fundamentals in the excited state and are excited up to 3 quanta. They therefore can be taken as totally symmetric vibrations. The former may be correlated with the a_{1g} (992 cm^{-1})-the ring breathing and the latter to be the b_{1u} (1010 cm^{-1})-the triogonal mode of benzene. This is in agreement with the assignments in several of the disubstituted benzenes studied. The excited state fundamentals 1272, 1537 cm^{-1} and 1250, 1550 cm^{-1} can be correlated with the infrared frequencies 1385, 1582 cm^{-1} and 1402, 1610 cm^{-1} in meta- and para-aminophenols respectively. They form combination with the other totally symmetric excited state fundamentals. Their frequent occurrence suggests that they can be taken as totally symmetric vibrations. In most of the analysed electronic spectra of disubstituted benzenes studied, frequencies around these values have been assigned to -C-C stretching mode. Accordingly they can be be correlated respectively with one of the totally symmetric components of e_{2u} (1485 cm^{-1}) and e_{2g} (1595 cm^{-1}) vibration in benzene in the excited electronic state. Fundamentals 345, 564 cm^{-1} and 436, 522 cm^{-1} in meta- and para-aminophenols respectively have been taken as the totally symmetric components of the e_{2g} (606 cm^{-1}) vibration in the excited state. The excited state fundamentals 345 and 436 cm^{-1} in meta- and para-aminophenols appear with $\Delta v = 3$ and also in combination with other fundamental vibrations with considerable intensity. They can be correlated respectively with the ground state frequencies 367, 620 cm^{-1} and 503, 581 cm^{-1} in the ultraviolet and 352, 620 cm^{-1} and 498, 581 cm^{-1} in the infrared spectra of meta- and para-aminophenols respectively. The *b*-component of this vibration in para- bromophenol and para-chlorophenol is at

632 and 635 cm^{-1} respectively. But in the vibrational spectra of para-aminophenol no infrared and Raman frequencies have been recorded near about 630 cm^{-1} and in the analysed vibrational spectra of para-aminophenol a frequency at 571 cm^{-1} has been assigned to this mode. So most probably this frequency 581 cm^{-1} in para-aminophenol may be correlated with b-component of 606 cm^{-1} e_{2g} vibration of benzene. The ground and excited state fundamentals 266, 206 cm^{-1} and 368, 301 cm^{-1} corresponding to the infrared frequency 242 and 370 cm^{-1} in meta- and para-aminophenols respectively may be ascribed to the -C-C out-of-plane bending mode.

The vibrations 1042, 1124, 1165 cm^{-1} and 1025, 1066, 1183 cm^{-1} involved in medium strong bands can be correlated with strong infrared bands at 1080, 1145, 1180 cm^{-1} and 1090, 1120, 1222 cm^{-1} in meta- and para-aminophenols respectively. They occur, in the case of some frequencies, up to two quanta and form combinations with the other totally symmetric vibrations. They may represent -C-H planar bending vibration corresponding to one of the totally symmetric components of e_{1u} (1030 cm^{-1}), e_{2g} (1178 cm^{-1}) and a_{2g} (1326 cm^{-1}) vibration in benzene in the excigted electronic state. Frequencies in this range in the halogenated phenols have been assigned to the -C-H in plane bending vibrations.

The excited state frequencies 1229 cm^{-1} and 1232 cm^{-1} in meta- and para-aminophenols which appear with medium intensity, forms combination bands with most of the frequencies of the excited state. It has been correlated with the infrared frequency at 1260 and 1248 cm^{-1}. This has been assigned as -C-OH stretching vibration in accordance with other substituted phenols. In the analysed vibrational spectra of these molecules frequencies 534, 222 cm^{-1} and 528, 352 cm^{-1} in meta- and para-aminophenols have been attributed to the -C-OH inplane bending and -C-OH out-of-plane bending vibrations respectively. Corresponding to this ground and excited state fundamentals i nmeta- and para-aminophenols are 535,508 cm^{-1}; 229,167 cm^{-1} and 528,473 cm^{-1}; 358,284 cm^{-1} respectively.

As may be seen from the tables 1 and 2 for meta- and para-aminophenols, most of the bands arise from the totally symmetric modes and the general vibrational structure of the absorption spectrum of the molecule in the vapour phase shows the well known characteristics of an allowed electronic transition.

The shifts of the 0, 0 bands from the position of 0, 0 of benzene are 3979 and 6696 cm^{-1} in meta- and para-aminophenols respectively. It is reported in the literature (Chandra & Tripathi 1963) that for weak interacting groups if both substituents are ortho-para directing or meta-directing groups, the order of the red shift is $o < m < p$. Since OH and NH_2 are all ortho-meta directing groups, the order of the red shift of 0, 0 bands of the mono-derivatives of phenol

studied must be $m < p$. The shift from meta ito para in this case is in keeping with this prediction.

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